

Study of the relation among Resist components, Outgassing species and Contamination



Yukiko Kikuchi, Toshiya Takahashi, Norihiko Sugie, Isamu Takagi
Kazuhiro Katayama, Eishi Shiobara, Hiroyuki Tanaka, Soichi Inoue
Takeo Watanabe*, Tetsuo Harada*, Hiroo Kinoshita*

EUVL Infrastructure Development Center, Inc. (EIDEC)

*Center for EUVL, University of Hyogo

Outline

■ Introduction and objective of this work

■ Experiments and results

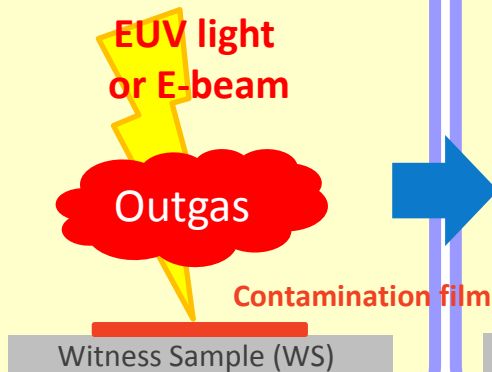
1. Identify the main contributors of outgassing components to carbon contamination.
2. Investigate the species of outgassing by Residual Gas Analyzer (RGA).
3. Compare EUV and E-beam.

■ Summary

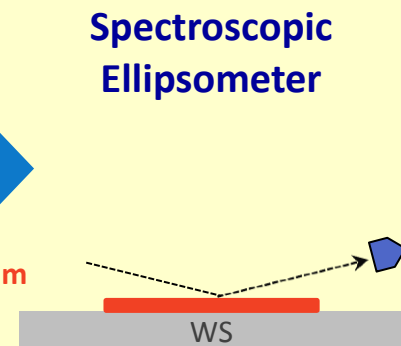
Introduction : Outgassing test requirement

- EUV resists must be passed the outgassing tests before being exposed in the EUV HVM scanner.
- Outgassing test source of either **EUV light or E-beam** are used to expose Resists and/or Witness samples (WS).
- OK judgment is given when the contamination film thickness and atomic% of non-cleanable element fall the certain critical values.

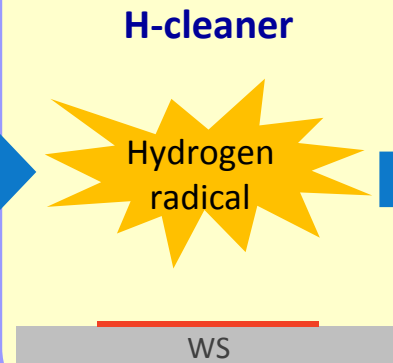
1. Contamination Growth (CG)



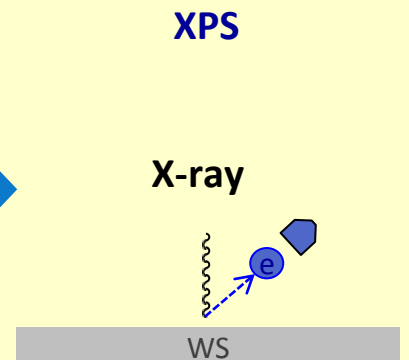
2. Film Thickness (FT) measurement



3. Hydrogen cleaning

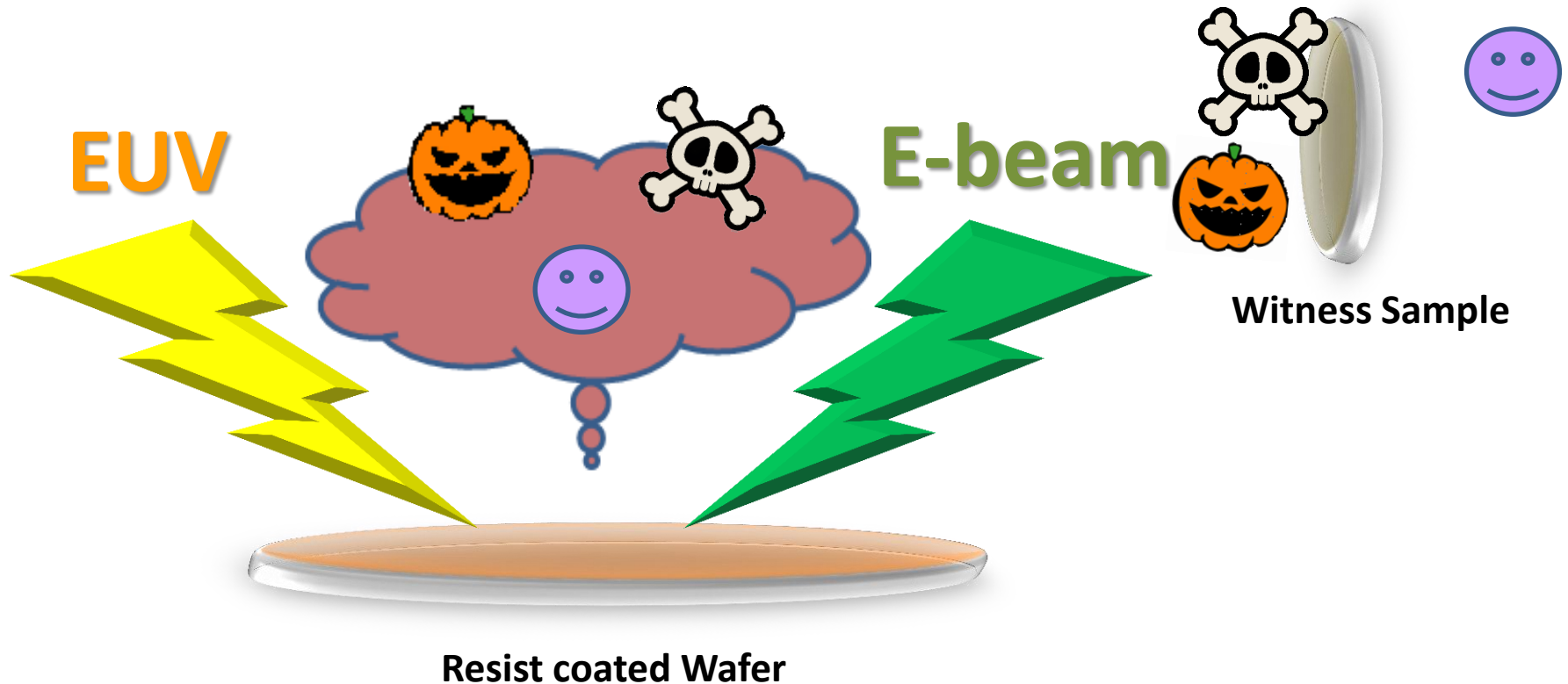


4. Non-cleanable element evaluation



Objective :

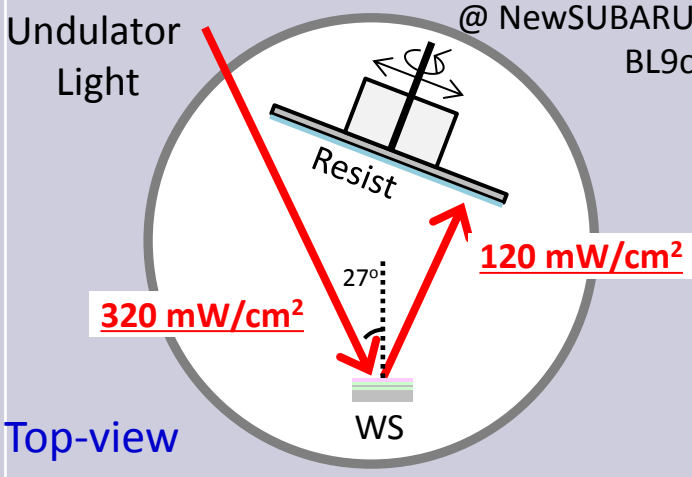
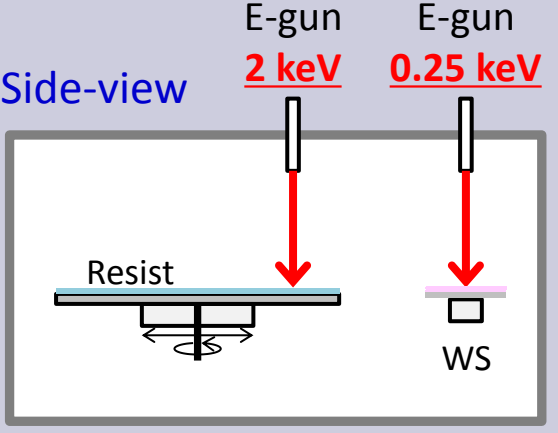
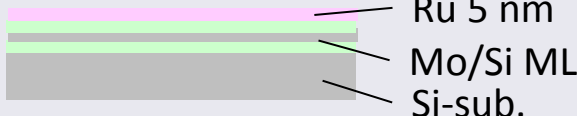
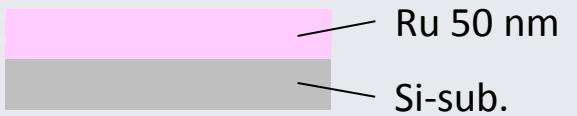
1. What species is the contributor of contamination?
2. Are the EUV and E-beam comparable?



Experiments

1. Get the breakdown of resist components in total contamination thickness by using the special sample set.
Each sample composed of the combination w/ or w/o of PAG and Protecting Unit (PU).
2. Identify the species of outgassing and carbon contamination by RGA.
3. Compare those results between EUV and E-beam exposure.

Outgas evaluation tool @ EIDEC

	High Power EUV - HERC* analysis tool -	Electron Beam (EB) - EUVOM-9000 -
Tool geometry	 <p>Undulator Light</p> <p>@ NewSUBARU BL9c</p> <p>Resist</p> <p>27°</p> <p>320 mW/cm²</p> <p>120 mW/cm²</p> <p>WS</p> <p>Top-view</p>	 <p>Side-view</p> <p>E-gun 2 keV</p> <p>E-gun 0.25 keV</p> <p>Resist</p> <p>WS</p>
Vacuum conditions	Base: $3 \sim 4 \times 10^{-6}$ Pa Exposure: $1 \sim 2 \times 10^{-5}$ Pa	Base: $3 \sim 4 \times 10^{-7}$ Pa Exposure: $2 \sim 4 \times 10^{-6}$ Pa
Resist thickness	60nm	
Witness Sample (WS)	 <p>Ru 5 nm</p> <p>Mo/Si ML</p> <p>Si-sub.</p>	 <p>Ru 50 nm</p> <p>Si-sub.</p>

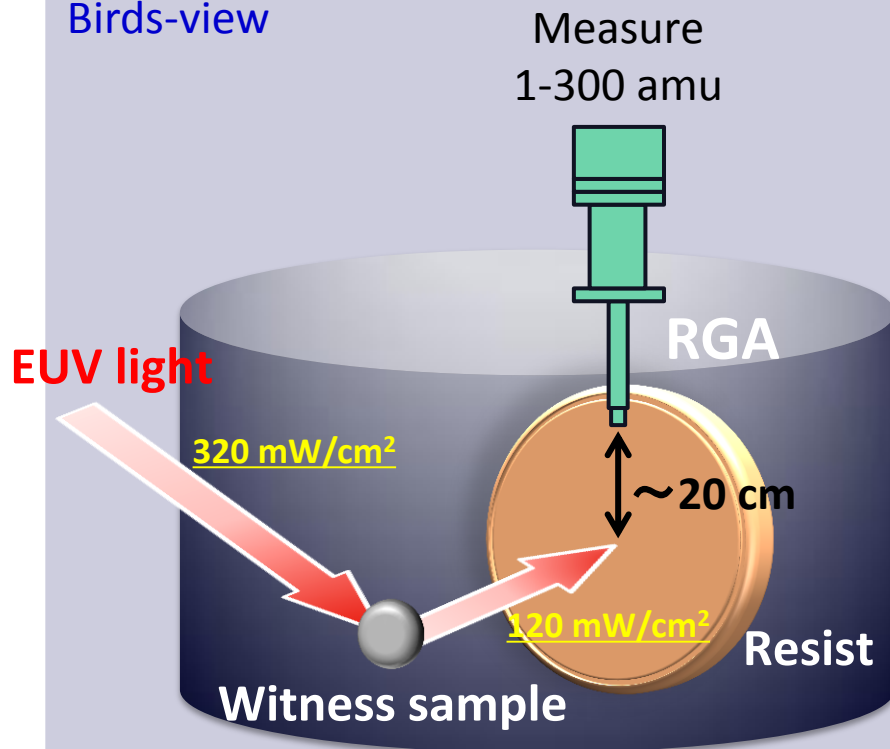
* HERC: High power EUV Resist Contamination

RGA measurement configuration

High Power EUV

HERC* analysis tool
@ NewSUBARU BL9c

Birds-view

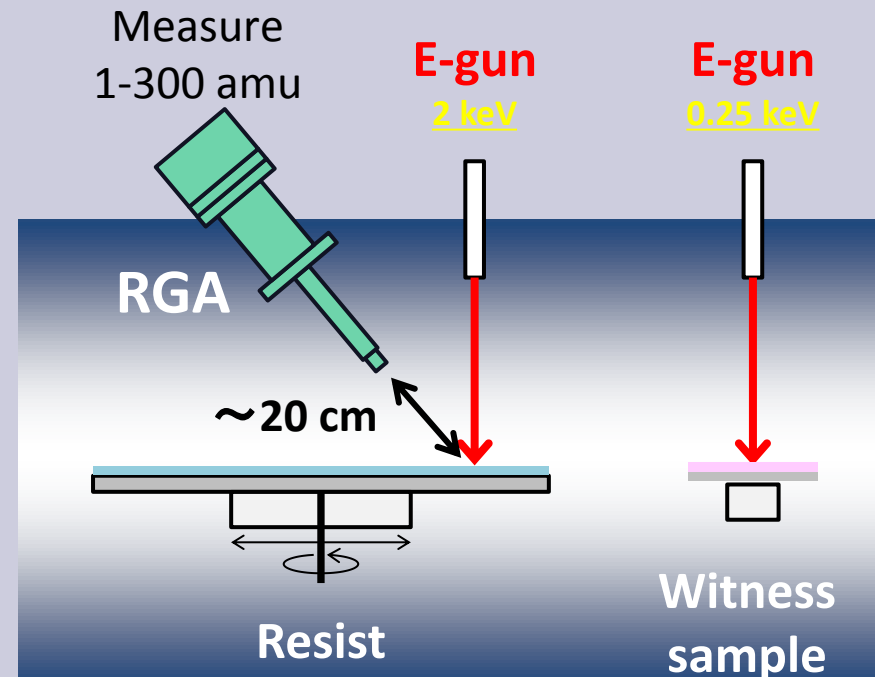


Expose 2 wafers ($200\text{mm}\phi$)
with $2.5 \times E_0$ and calibrate for a
 $300\text{mm}\phi$ wafer

Electron Beam (E-beam)

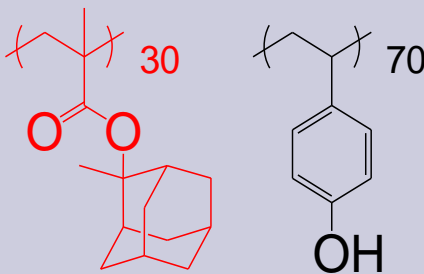
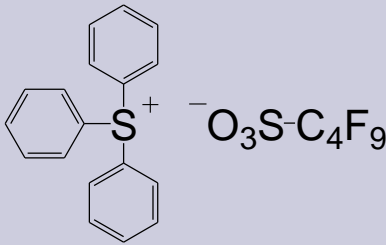
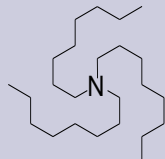
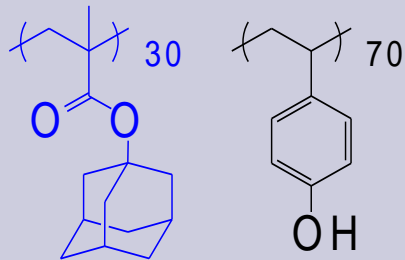
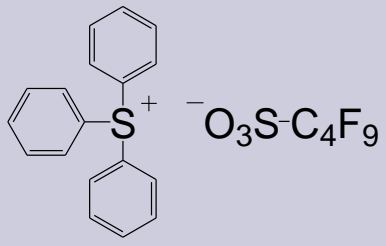
EUVOM-9000
@ EIDEC

Side-view



Expose 1 wafer ($300\text{mm}\phi$)
with E_0 (60 min x1)

Sample Set composition

Sample Concept	Polymer	PAG (20wt% of polymer)	Quencher (0.1mol of PAG)
Model Resist			 Tri-n-octylamine
PAG free	Acid labile unit	none	
PU free			
PAG and PU free	Acid stable unit	none	

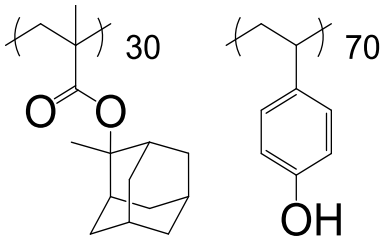
Outgassing source of each sample

Sample Concept	Polymer	PAG (20wt% of polymer)	Possible Source of Contamination
Model Resist	<p>Acid labile unit</p>		<ul style="list-style-type: none"> ▪ Polymer ▪ Protecting Unit ▪ PAG ▪ Background
PAG Free	<p>Acid labile unit</p>	none	<ul style="list-style-type: none"> ▪ Polymer ▪ Directly decomposed Protecting Unit ▪ Background
PU Free	<p>Acid stable unit</p>		<ul style="list-style-type: none"> ▪ Polymer ▪ PAG ▪ Background
PAG and PU Free	<p>Acid stable unit</p>	none	<ul style="list-style-type: none"> ▪ Polymer ▪ Background

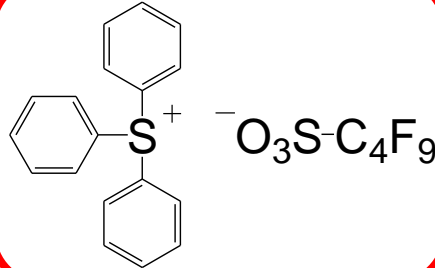
Model Resist Outgassing mechanism and measured contamination

Model Resist

Polymer



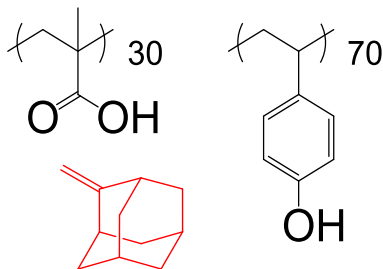
PAG



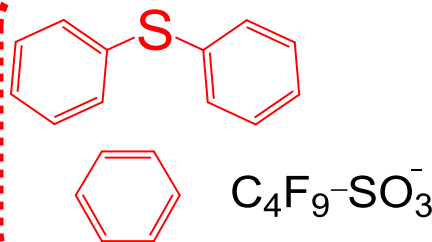
Chemical decomposition

Photo (Radiation) decomposition

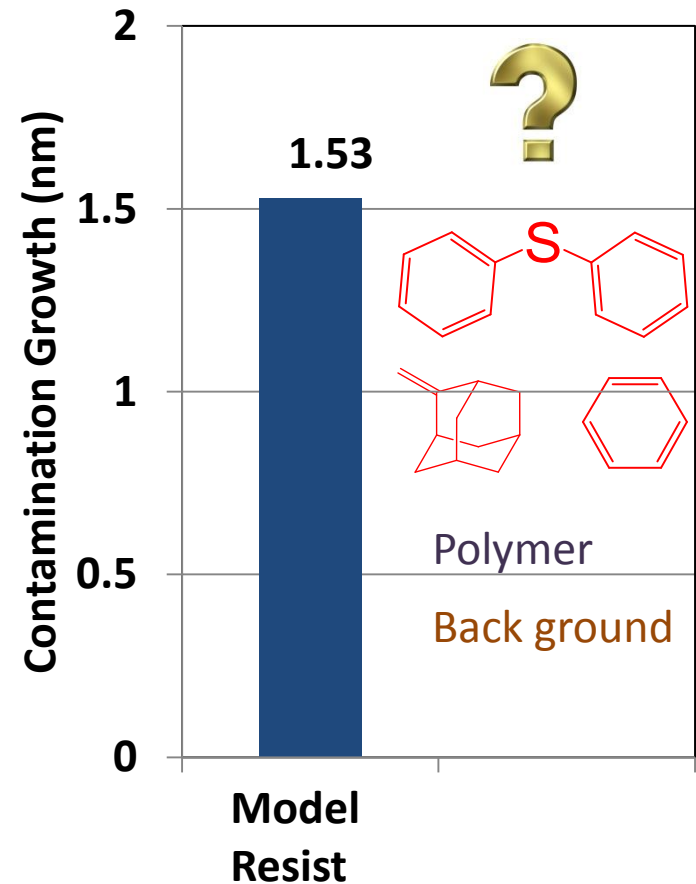
Decomposition



De-protected Unit

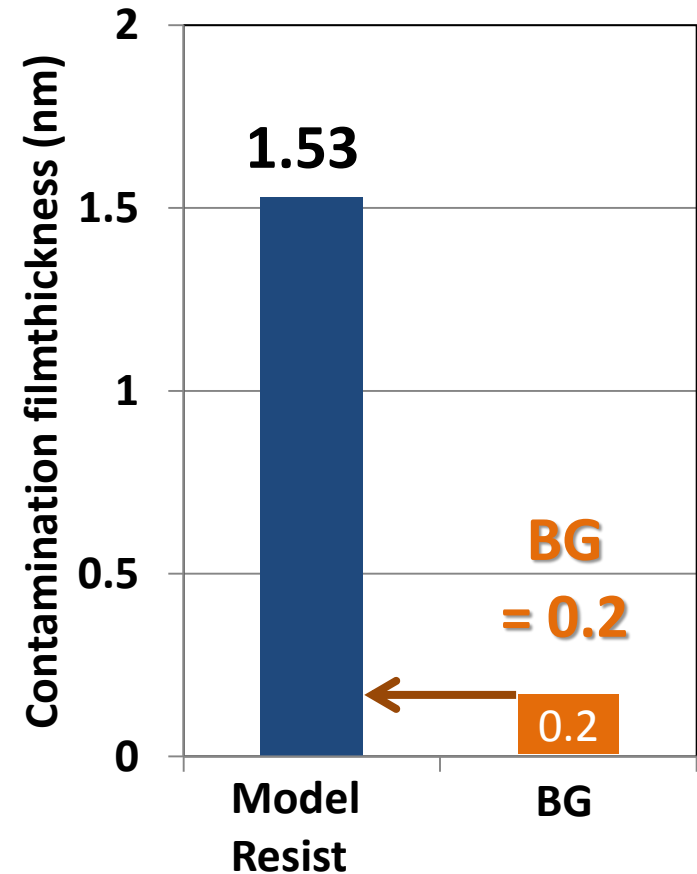
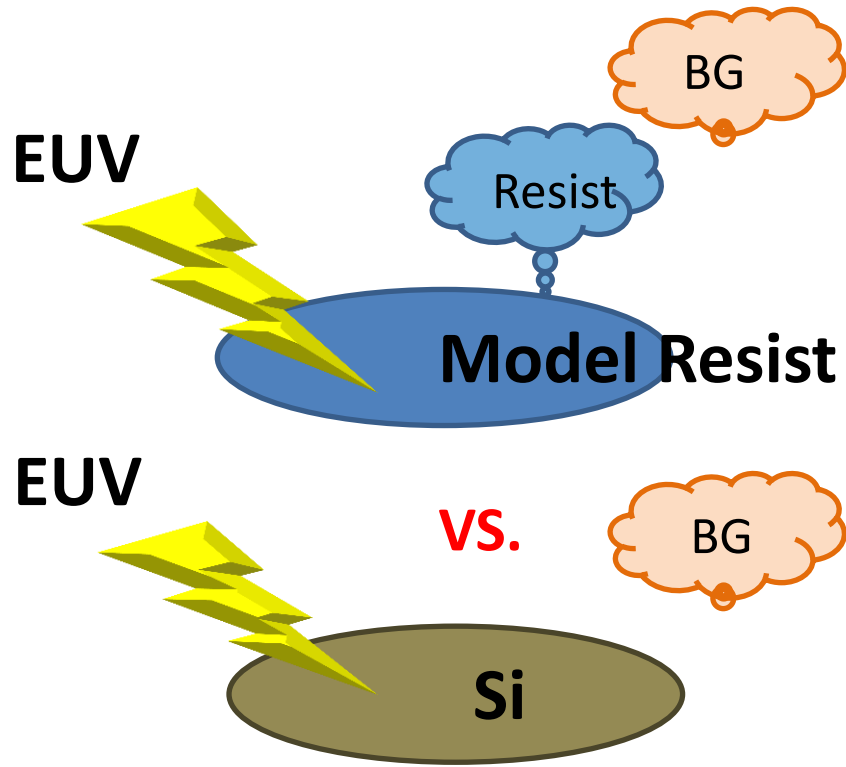


Decomposed PAG



■ How much is the contribution of each outgassing species?

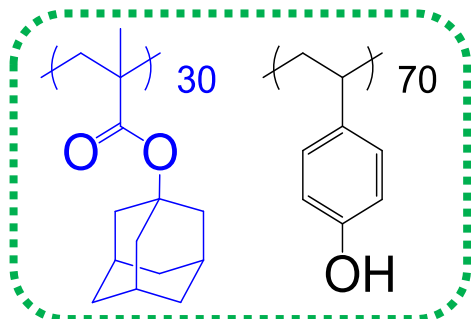
Contribution of Background (BG) Atmosphere in Contamination Thickness



■ Contribution of **Background** in Contamination Thickness is **0.2 nm**.

Contribution of base polymer

PAG and PU free composition



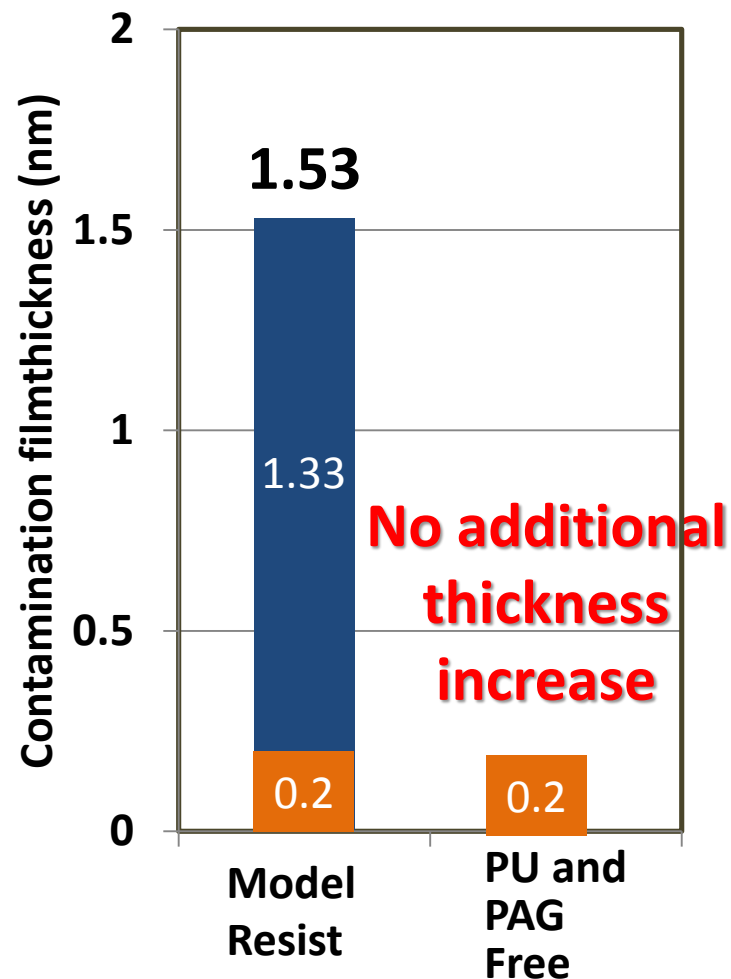
Acid stable unit

no PAG

Polymer

~~**Protecting Unit**~~

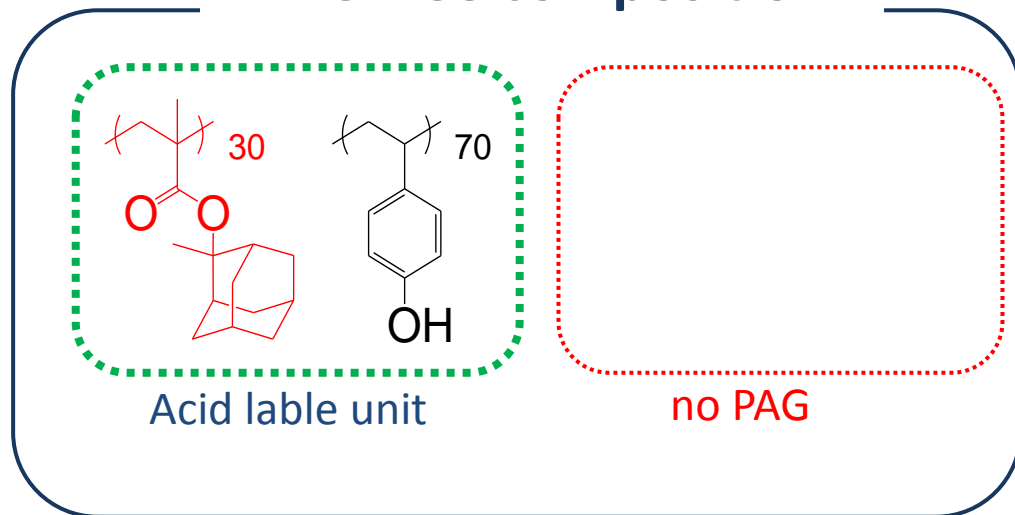
~~**PAG**~~



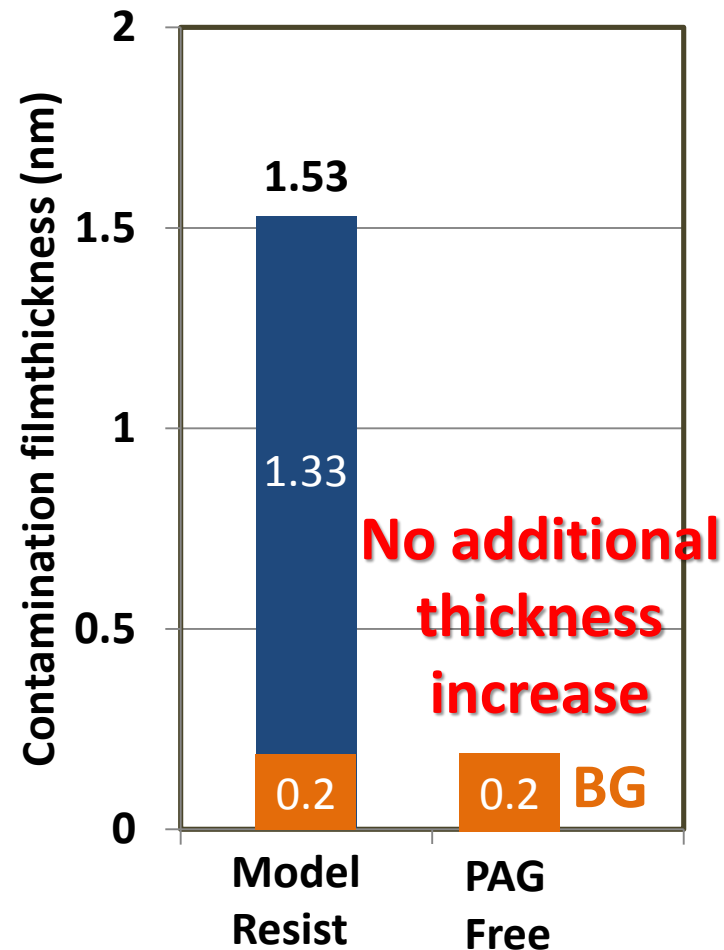
■ Negligible contribution from polymer.

Contribution of PU direct decomposition w/o PAG

PAG free composition



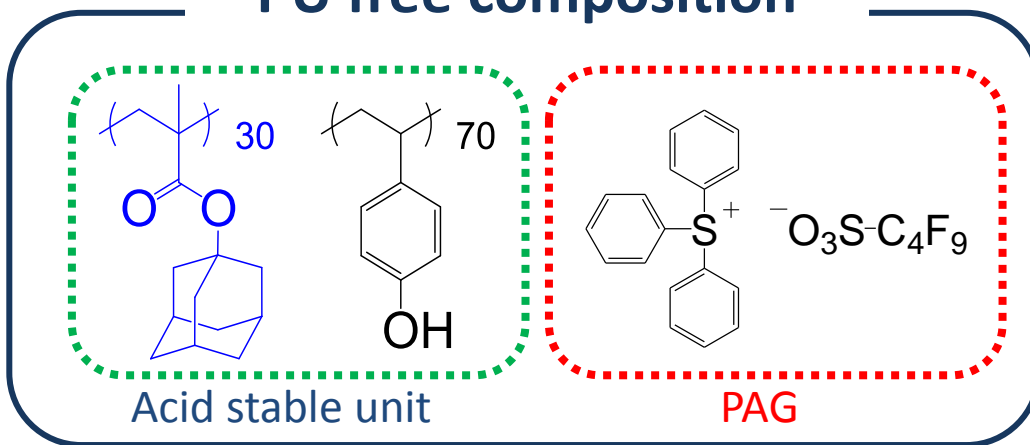
**Polymer
Protecting Unit
~~PAG~~**



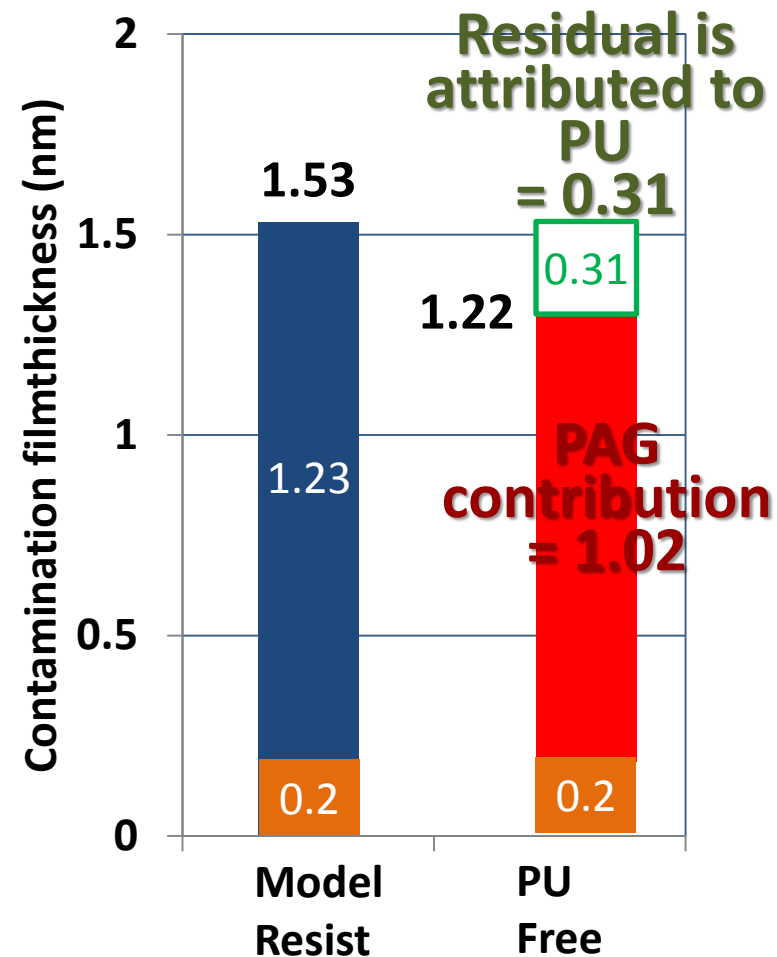
■ Negligible contribution from
PU direct decomposition.

Contribution of PAG and PU

PU free composition



Polymer
~~Protecting Unit~~
PAG

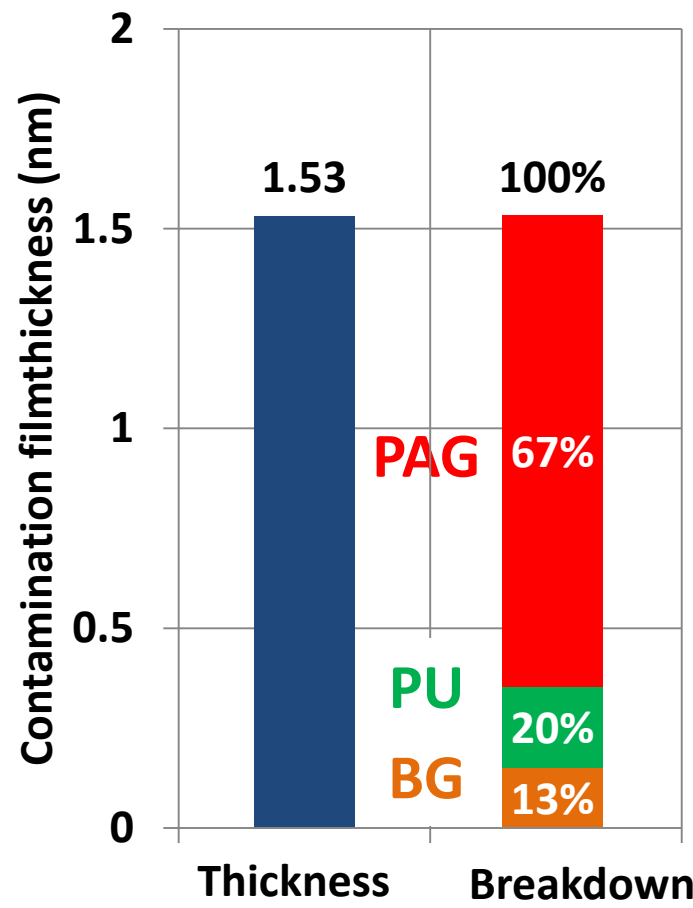
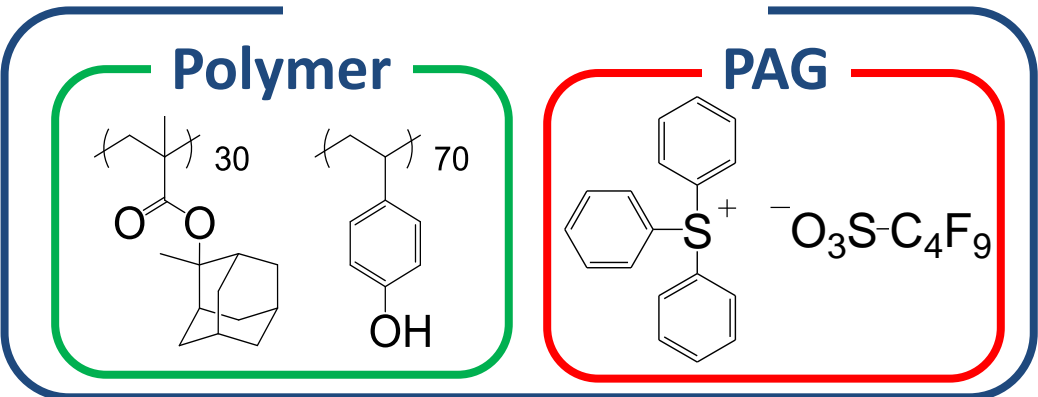


■ Contribution of PAG : $1.22 - 0.20 = 1.02 \text{ nm}$

■ Contribution of PU : $1.53 - 1.22 = 0.31 \text{ nm}$

Summary 1 : Contamination Thickness composition by EUV

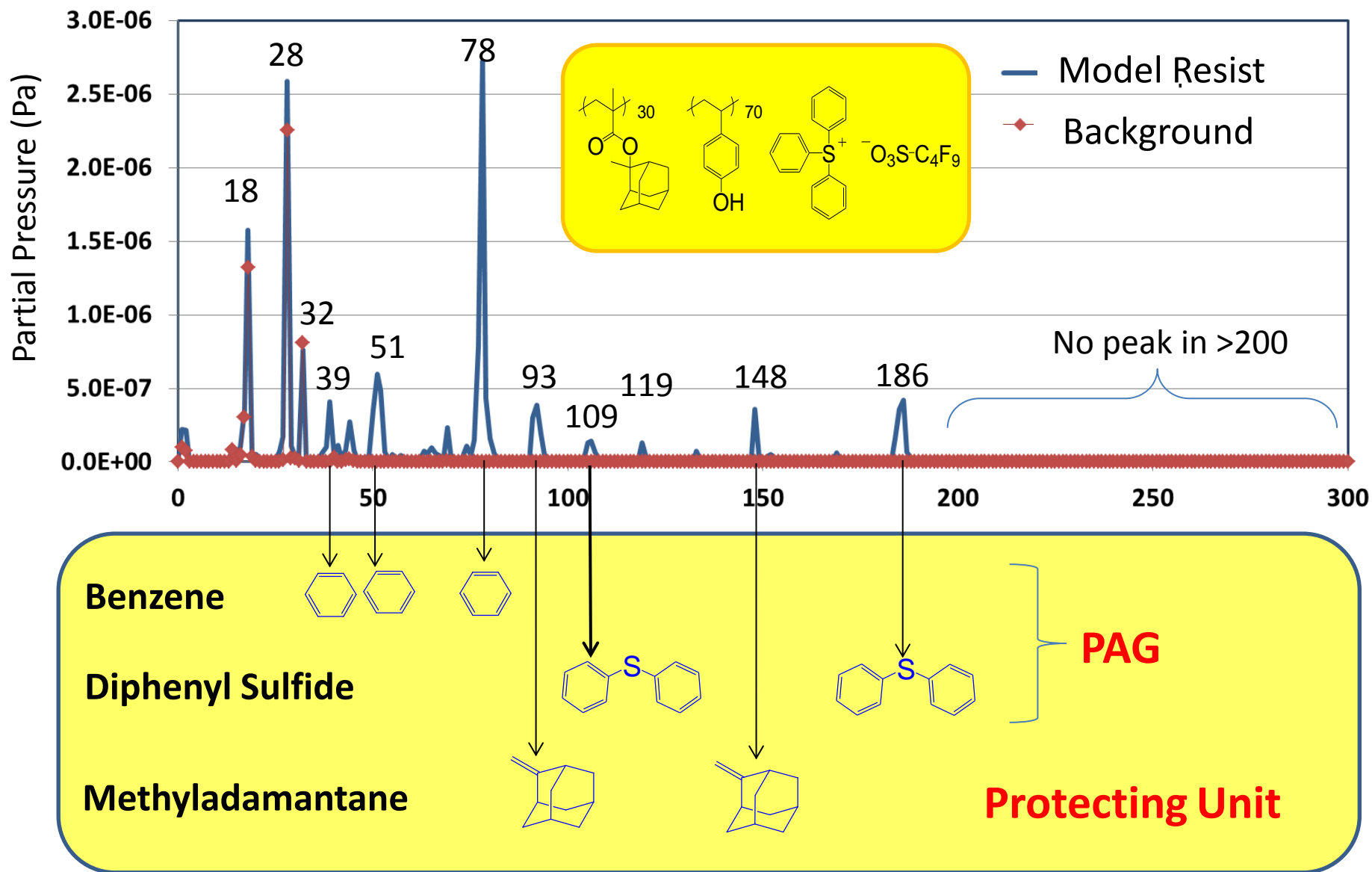
Model Resist



■ ~70% of the Contamination Thickness is by PAG component

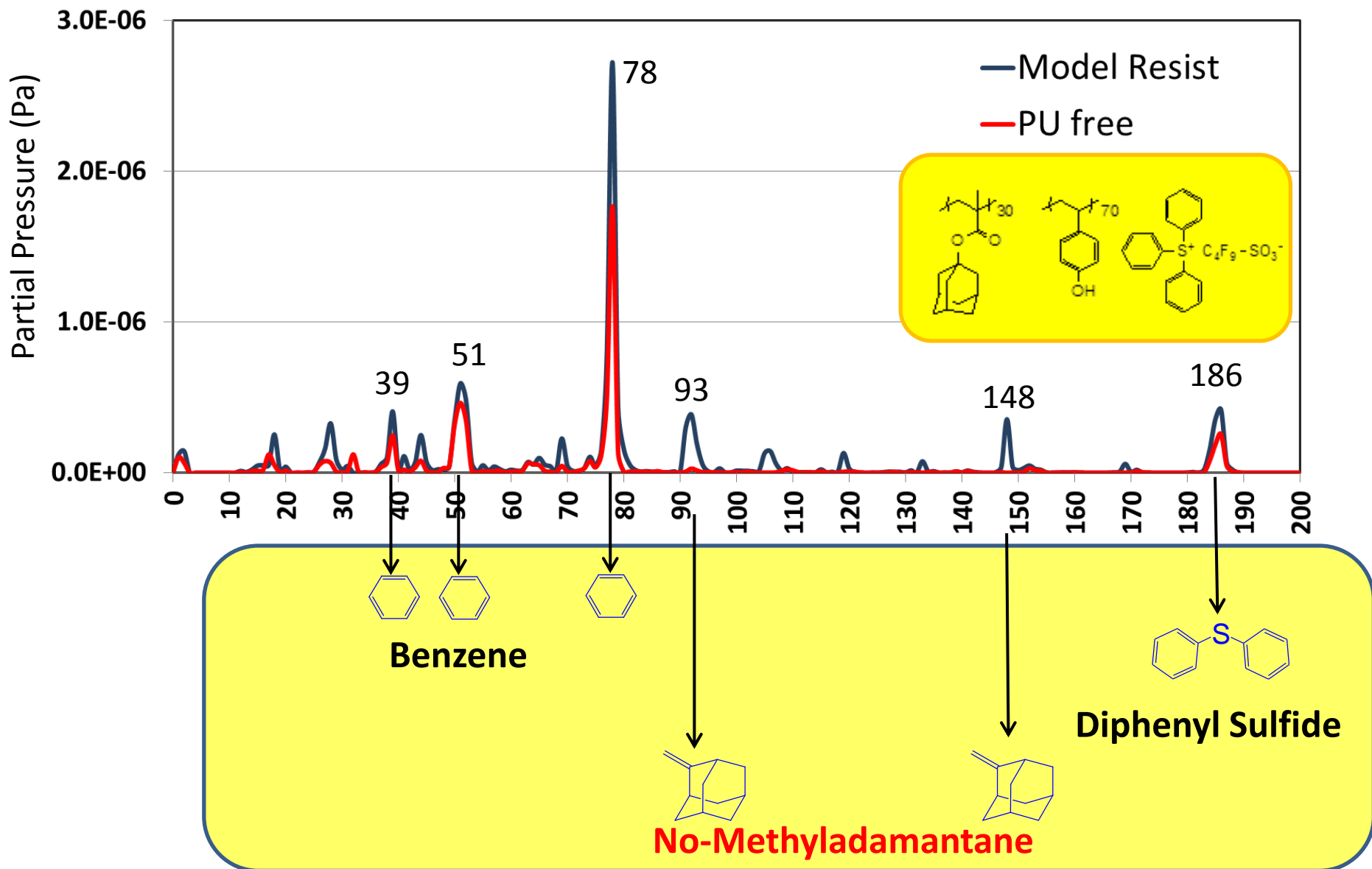
What species are found in RGA ?

RGA Spectrum of Model Resist

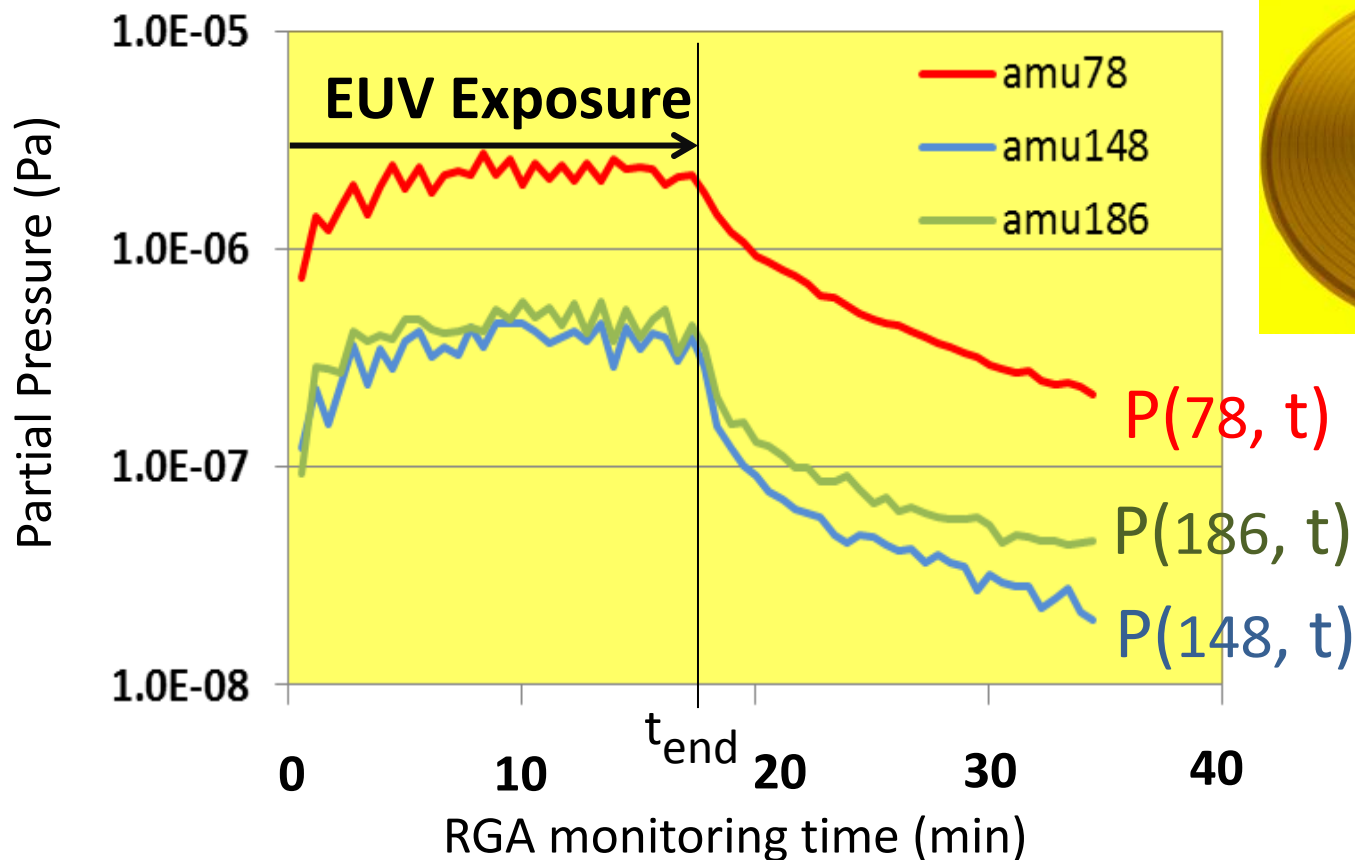


RGA Spectrum of **PU free sample** (Contribution of PAG)

Back Ground is subtracted



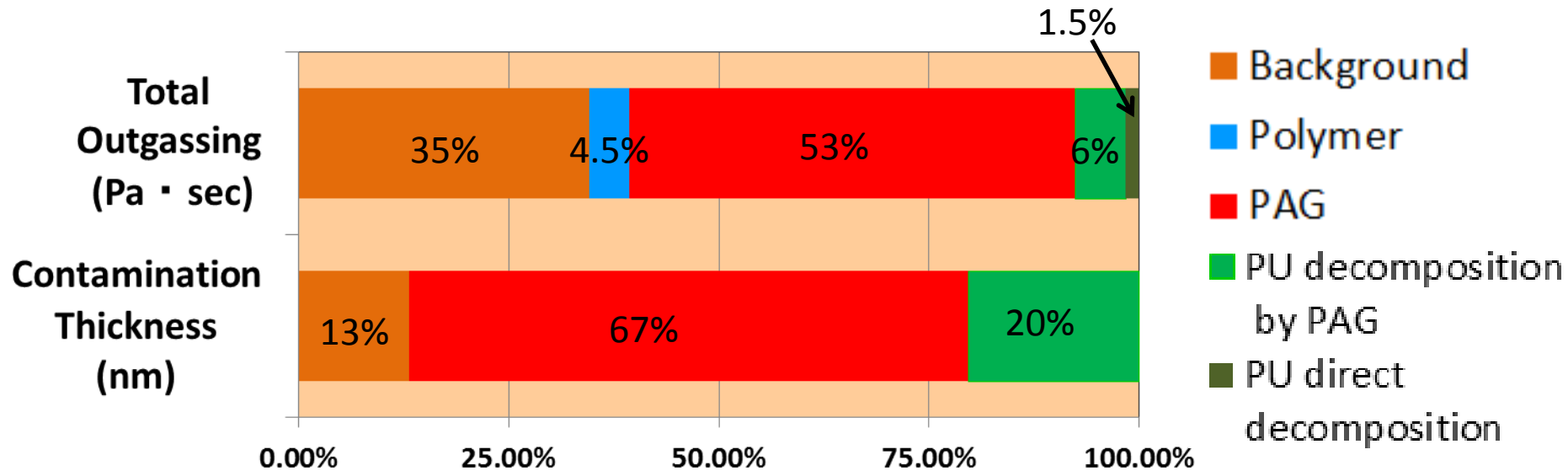
Total outgassing calculation



Partial Pressure change during the exposure of a 200 mm wafer with the Model Resist by EUV

Total Outgassing :
$$P_{\text{sample}}(\text{total}) = \sum_{t=0}^{t_{\text{end}}} \sum_{\text{amu}=1}^{300} P(\text{amu}, t) \times \text{factor for a 300mm wafer}$$

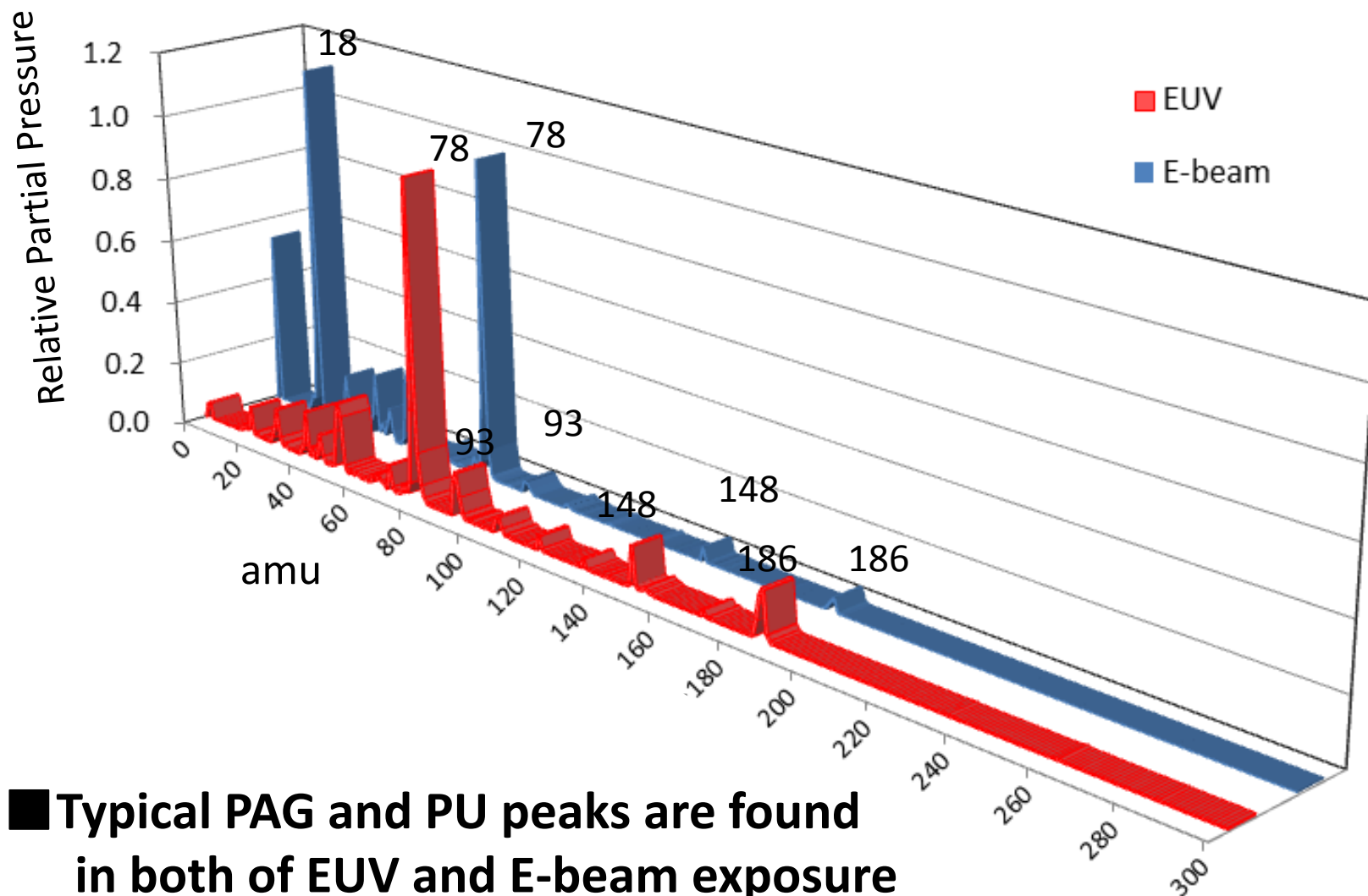
Summary2: Composition of Outgassing and Contamination thickness by EUV exposure



- Gas volume of PAG is **about half in total amount** but contribution in the **contamination is about 70%.**
- Polymer is also outgassing but does not make contribution to the contamination
- Outgassing from the **PU direct decomposition** is detected. But it is **very small**, and not be seen in contamination thickness.

Comparison between EUV and E-beam

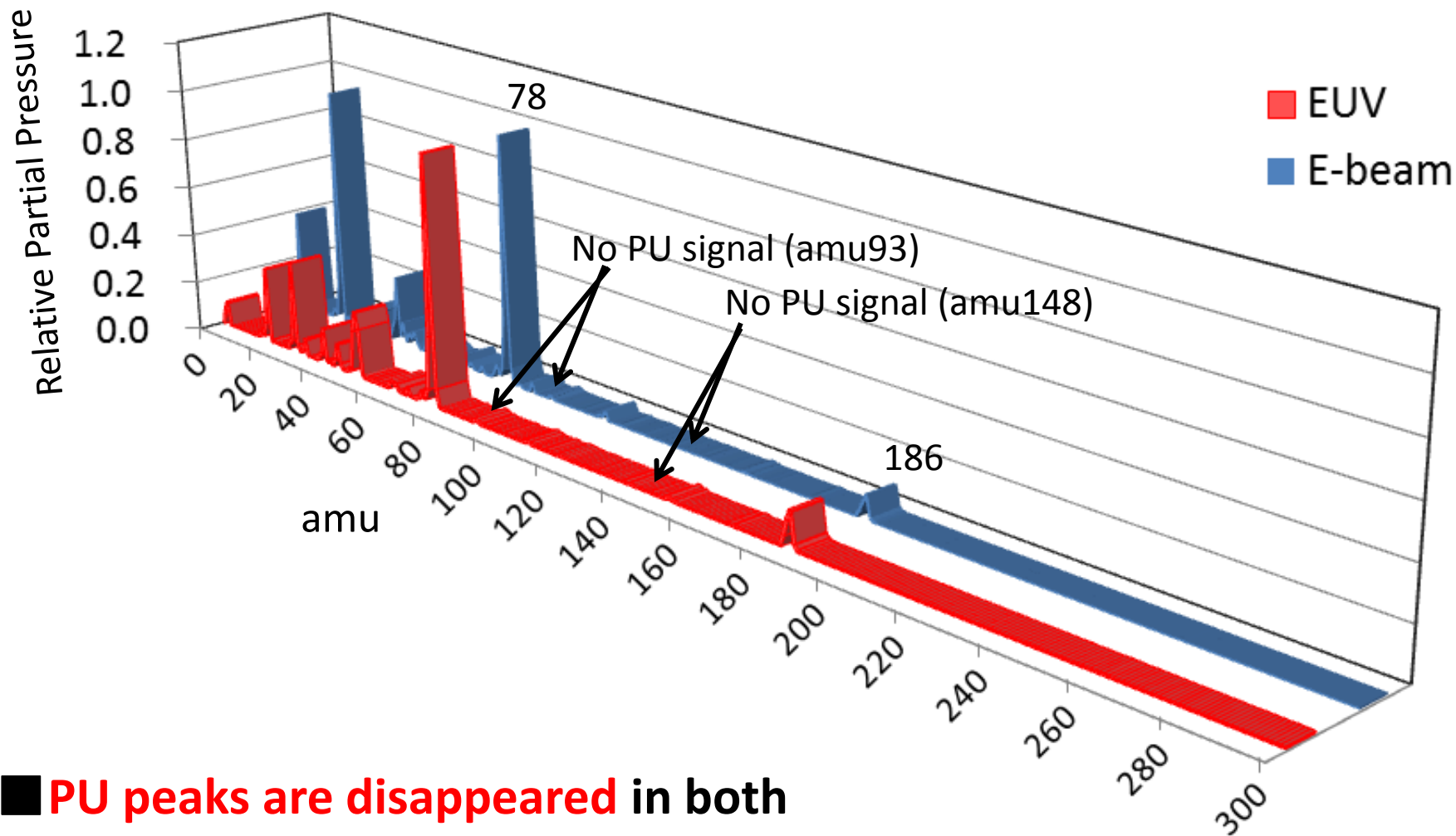
RGA signals of Model Resist by EUV and E-beam



■ Typical PAG and PU peaks are found in both of EUV and E-beam exposure

Normalized at the peak of amu78
BG are subtracted

RGA signals of PU free sample by EUV and E-beam



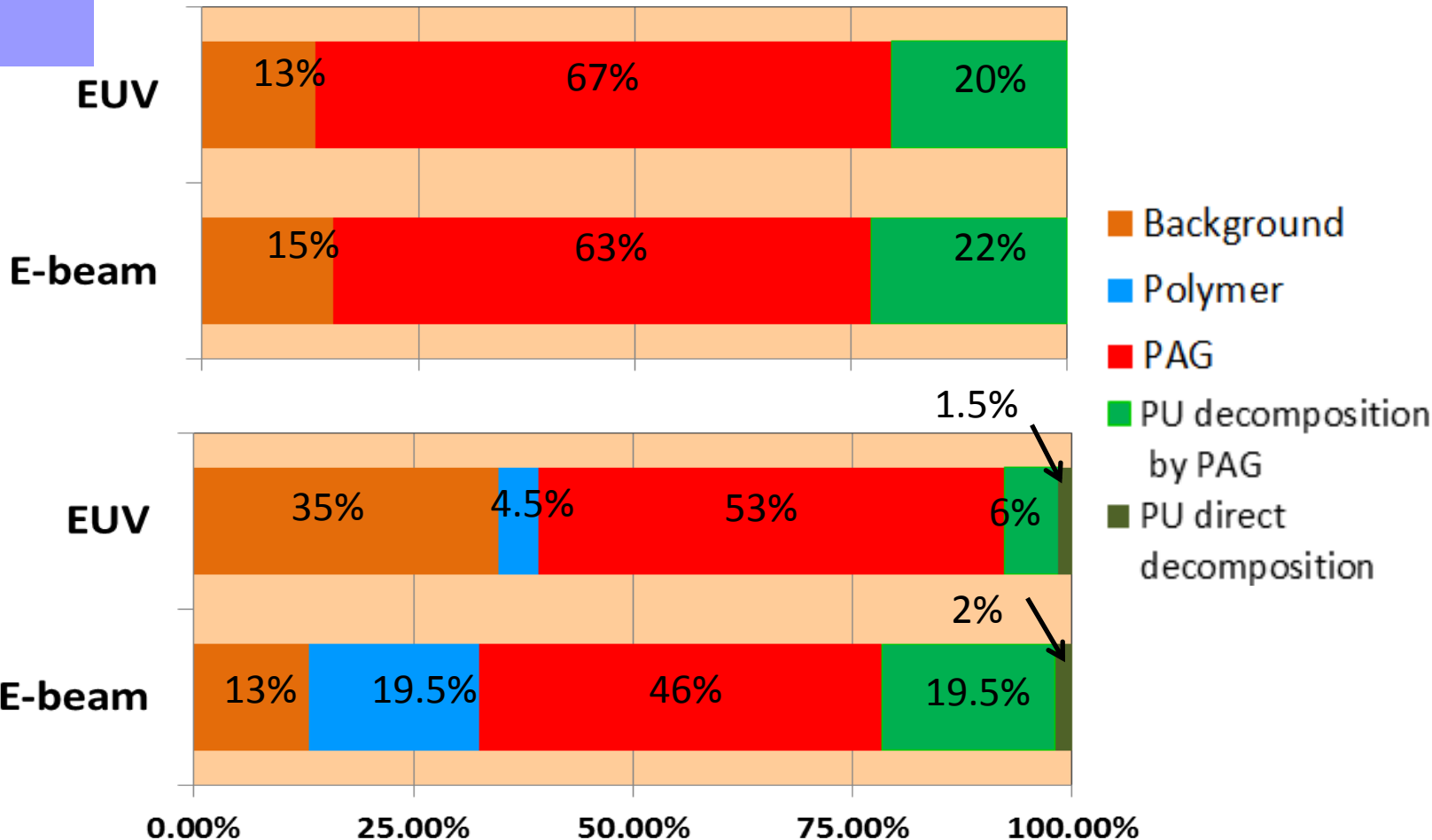
■ **PU peaks are disappeared** in both of EUV and E-beam exposure.

Normalized at the peak of amu78
BG are subtracted

Summary3: Composition of Outgassing and Contamination

Thickness by EUV and EB

Contamination
Thickness



The PAG and PU contribution in Contamination thickness are same in EUV and E-beam. But the composition of total outgassing amount shows difference.

Summary

- Using the samples with different combination of resist components, the contribution of each components in the contamination thickness were investigated.

PAG contribution was 60~70% , and
PU contribution was ~20%
in both of EUV exposure and E-beam exposure.

- Most of the characteristic RGA peaks of PAG and PU were same in EUV and E-beam exposure.
But the peak ratio and total gas amount showed a little discrepancy.
We will study further on this finding.

Acknowledgment

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